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Catalytic cracking of mixtures of model bio-oil compounds and gasoil

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A B S T R A C T

Key model bio-oil O-compounds representing some of the major oxygenate groups, such as acetic acid, hydroxyacetone and phenol, were mixed with a standard gasoil and tested under fluid catalytic cracking (FCC) conditions in a laboratory-scale unit using an industrial FCC equilibrium catalyst (E-CAT) and a mixture of E-CAT and ZSM-5 additive. As a general trend, acetic acid, phenol or hydroxyacetone when mixed with a conventional gasoil increased the overall conversion, defined as fraction of the feed converted into gases, gasoline and coke, reduced the coke yield and increased fuel gas, LPG and gasoline. The conversion of the gasoil itself over pure E-CAT was not altered significantly by the presence of these compounds. This result could be interpreted by a preferential adsorption of the feed on the catalytic surface instead of the oxygen containing compounds. On the other hand, the ZSM-5 additive effect was attenuated in the presence of the O-compounds, suggesting a preferential interaction of such compounds with the ZSM-5. Up to 10 wt.% of these O-compounds studied can be processed without major problems in a FCC unit except for phenol.

1. Introduction

Nowadays, crude oil resources limitations, as well as the need for a drastic reduction of air pollution, have caused a strong interest for the development of new bases for liquid fuels production. In this context, lignocellulosic biomass material seems to be a potential renewable energy source. To be used as a refinery feedstock, this biomass needs to be liquefied. The two major technologies to convert the biomass into oils, denominated bio-oils, are pyrolysis and liquefaction [1–4].

The bio-oils chemical properties are significantly different from that of petroleum feedstocks. In fact, bio-oils are a complex mixture of water (15–30 wt.%) and different O-containing structures (35–50 wt.%), such as hydroxyaldehydes, hydroxyketones, sugars, carboxylic acids and phenols. Due to their oxygen-rich composition, they present low heating value, immiscibility with hydrocarbon fuels, chemical instability, high viscosity, corrosiveness, etc. [1,5–9]. Therefore, it is necessary to transform the bio-oils oxygen molecules into more suited compounds to act as fuel.

Many studies concerning the conversion of the bio-oils were performed using zeolites [10–18] or mesoporous materials [14,19–22] as catalysts. Adjaye and Bakhshi [13,14] tested different types of catalysts (H-ZSM-5, H-Y, H-mordenite, silicalite and silica alumina) for the upgrading of bio-oil produced from wood. Acidic zeolite catalysts revealed to be more effective in the bio-oil conversion to hydrocarbons. The transformation of different bio-oil model compounds, including aldehydes, ketones, acids, alcohols, phenols and mixtures, over H-ZSM-5 catalysts was also studied by Adjaye and Bakhshi [11] and Gayubo et al. [15–17]. They observed that the studied families presented great differences in their reactivity and each presented a particular reaction pathway. The temperature had also an influence in the products distribution. Generally, the catalytic cracking catalysts have shown great ability to remove the O-compounds and convert them into CO, CO_2, H_2O and hydrocarbons. Therefore, according to Chen et al. [23], that studied the carbohydrates transformation over H-ZSM-5 zeolites, the key problem in this conversion was to remove the oxygen function without compromise the hydrogen content of the liquid product, which allows improving its combustion properties. In this respect, they defined an effective hydrogen index,

$$\left(\frac{H}{C}\right)_{\text{eff}} = \frac{H-2O-3N-2S}{C}, \quad (1)$$

where H, C, O, N and S are the moles of hydrogen, carbon, oxygen, nitrogen and sulphur, respectively. It is evident that biomass-derived feedstocks have a lower H/C_{eff} ratio than petroleum charges, in consequence of the higher oxygen content.

Since the existence of dedicated fluid catalytic cracking units for bio-oils is still under development, a possible alternative for the

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Table 1
Physicochemical properties of the tested catalysts.

	E-CAT	ZSM-5 additive
SiO_2 (wt.%)	–	59.6
Al_2O_3 (wt.%)	41.2	22.8
Na_2O (wt.%)	0.49	0.17
RE_2O_3 (wt.%)	2.35	–
Ni (ppm)	1559	–
V (ppm)	1820	–
Surface area ($m^2\,g^{-1}$)	164	133
V_{micro} ($cm^3\,g^{-1}$)	0.056	0.039

Table 2
Characterization of the reference feed.

Properties	FCC gasoil
Density ($g\,cm^{-3}$)	0.952
API gravity	16.5° API
Aniline point (°C)	72.5
Basic N UOP269 (ppm)	1307
Total N (wt.%)	0.325
Total S (wt.%)	0.712
RCR (wt.%)	1.23
ASTM 1170 (°C)	
IBP	291
10%	381
30%	431
50%	461
70%	494
90%	535
FBP	621

near future is co-feeding the bio-oils with the FCC feedstocks [24–26]. Indeed, Corma et al. [25] and Dupain et al. [26] demonstrated that some O-compounds can be converted together with vacuum gasoil without radically altering the products selectivity.

Fluid catalytic cracking (FCC) is one of the most important processes of a modern refinery because of its flexibility to changing the feedstock and product demands. Its principal aim is to convert high-molecular-weight hydrocarbons to more valuable products, mainly gasoline [27–30]. The typical FCC catalyst consists of a mixture of an inert matrix (kaolin), an active matrix (alumina), a binder (silica or silica–alumina) and a Y-zeolite [28,30]. Due to the increasing propylene demand, ZSM-5 has been used as an additive with the purpose to enhance the light olefins production [31,32]. Its utilization also allows improving the octane number of gasoline by favouring the cracking and isomerization of low-octane compounds into lighter and more branched products [33–35].

In this work, key model bio-oil O-compounds representing some of the major oxygenate groups, such as acetic acid, hydroxyacetone and phenol, were added to a standard FCC unit feed, in order to reproduce the bio-oils co-feeding. Their influence on the conversion, products yield and catalyst deactivation is investigated, using an industrial FCC equilibrium catalyst (E-CAT) and a mixture of E-CAT and ZSM-5 additive.

2. Experimental

The catalysts used in this study were an industrial FCC equilibrium catalyst (E-CAT) and a mixture of 90% E-CAT and 10% ZSM-5 additive. The additive was deactivated separately at 788 °C under a 100% steam atmosphere, in a laboratorial fix bed unit. Both samples were supplied by PETROBRAS. Some physico-chemical characteristics of the materials used are shown in Table 1.

As reference feedstock, a commercial FCC gasoil from PETROBRAS was used. Its main characteristics are presented in Table 2. To simulate the bio-oils co-processing, different samples were prepared by mixing this gasoil with the same mol% of each model oxygenate compound. The prepared feedstocks contained 10.0 wt.% of phenol (Vetec, 99%), 6.6 wt.% of acetic acid (Vetec, 99.7%) and 8.0 wt.% of hydroxyacetone (Sigma–Aldrich, 90%).

The catalytic tests were performed in a fixed-fluidized-bed ACE® unit [27]. The reaction was carried out in a steel reactor at 535 °C under atmospheric pressure. The reactor feed was constituted by a nitrogen top stream of 40 ml min^{-1}, a nitrogen bottom stream of 100 ml min^{-1} and a feedstock stream of 1.20 g min^{-1}, which were maintained constant. Catalyst-to-oil ratio (CTO) values of 3, 5, 7 and 9 were achieved by means of changing the feedstock injection times. In all experiments, the catalyst mass was kept constant and equal to 9 g, in order to obtain a contact time similar to the FCC riser.

The liquid and gaseous effluents were collected in a condenser and a gas bottle, respectively. After the reaction, the catalyst was stripped with 140 ml min^{-1} of nitrogen for 350 s. The liquid was also stripped with 20 ml min^{-1} of nitrogen for a period that is function of the CTO (7× injection time).

After the catalytic experiment, in situ catalyst regeneration was done to determine the coke content. This step was carried out at 695 °C under air flow (120 ml min^{-1} at the top and 100 ml min^{-1} at the bottom). A Pt/SiO_2 catalytic converter (535 °C) was used to transform the CO secondarily formed in CO_2. The total CO_2 was analyzed by IR spectroscopy with a Servomex 1440 Gas Analyser.

The liquid effluent was analyzed by simulated distillation with an Agilent 6890 gas chromatograph, using a HP-1 methyl silicon column and a flame ionization detector. The gasoline, light cycle oil (LCO) and decanted oil (DO) were quantified considering the temperature ranges of <216 °C, 216–344 °C and >344 °C, respectively.

An Agilent 3000A micro gas chromatograph, equipped with four columns (Molecular Sieve 5A Plot, Plot U, Alumina Plot and OV-1) and four thermal conductivity detectors, was used to analyze the gaseous effluent (H_2, C_1–C_5^+).

The yields were calculated as the weight percent of reactant. Conversion is defined as $X = 100\,(\text{wt.\%}) - \text{LCO}\,(\text{wt.\%}) - \text{DO}\,(\text{wt.\%})$. The obtained results were analyzed by statistical methods and the runs corresponding to the detected outlier points were repeated.

To have a detailed characterization of the gasoline fraction composition, the liquid product was submitted to the PIANIO method, which allows determine the paraffins, iso-paraffins, aromatics, naphthenes, iso-olefins and olefins content. It was used an Agilent 6890N gas chromatograph, with a PONA methyl silicon column and a flame ionization detector.

For each type of feed and catalyst, the liquid effluents were submitted to GC–MS and GC-FID (PIANIO), at the same analysis conditions, in order to analyze the oxygenated compounds formed. The O-compounds present in the liquid effluents were qualitatively determined by GC–MS coupling with an HP 5973N, using a DB-5 methyl phenyl silicon capillary column and, then, quantified by PIANIO analysis.

The water content in the liquid effluent was measured with an automatic Metrohm 756 KF coulometer, using the columetric Karl Fischer method.

3. Results and discussion

3.1. E-CAT

Based on the conversion *vs.* CTO curves (Fig. 1a), it could be observed an increase in conversion when the model oxygenated compounds are added to the gasoil. This indicates that acetic acid, phenol or hydroxyacetone do not increase the residual fractions, LCO (Fig. 1g) and DO (Fig. 1h).

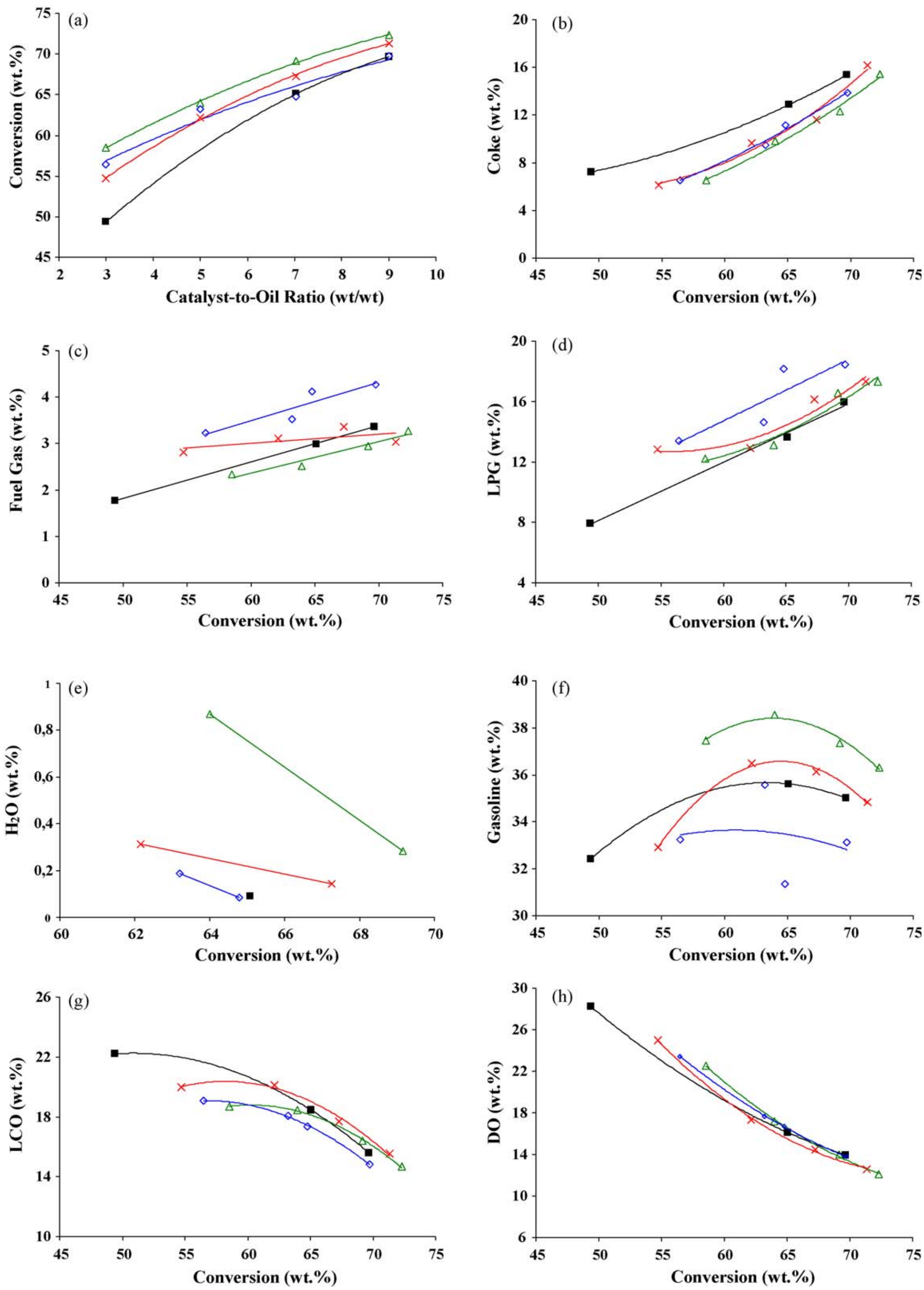


Fig. 1. (a) Conversion *vs.* CTO, (b) coke, (c) fuel gas, (d) LPG, (e) H_2O, (f) gasoline, (g) LCO and (h) DO *vs.* Conversion, for pure gasoil (■), gasoil + phenol (△), gasoil + acetic acid (◇) and gasoil + hydroxyacetone (×) mixtures with E-CAT.

Considering the difference between the conversion for the mixture and the conversion based on the percentage of gasoil present in the mixture, the average results obtained were 11.5, 7.0 and 8.1 wt.%, respectively for phenol, acetic acid and hydroxyacetone. The values founded are similar to the percentages of these oxygenated compounds in the mixtures (10.0, 6.6 and 8.0 wt.%, for phenol, acetic acid and hydroxyacetone). This strongly indicates that the observed increase in the total conversion for the mixtures is only due to an additive effect of the conversion of the gasoil and the presence of the O-compounds (boiling point in gasoline range) and their products. These products could be either of lower molecular weights or coke.

We would now further analyze the formation of coke. Due to the polar nature of oxygenated compounds and in agreement with

previous published papers [11,12,15,16,24], they tend to form large amount of coke over acid catalysts. Surprisingly, this was not observed in the present work. Fig. 1b shows the results of coke yield *vs.* conversion and there is a very clear reduction trend for coke in the presence of oxygenated compounds. This result could be explained if coke-tendency of the gasoil is higher than that of the model compounds, in such case, partially replacing the gasoil by the oxygenated compound indeed helps.

Actually, both the behaviours of conversion and coke yields could make sense if competitive adsorption is considered. First, the average molecular weight of the gasoil molecule is much higher than the O-compound being co-processed. Further, in the gasoil,

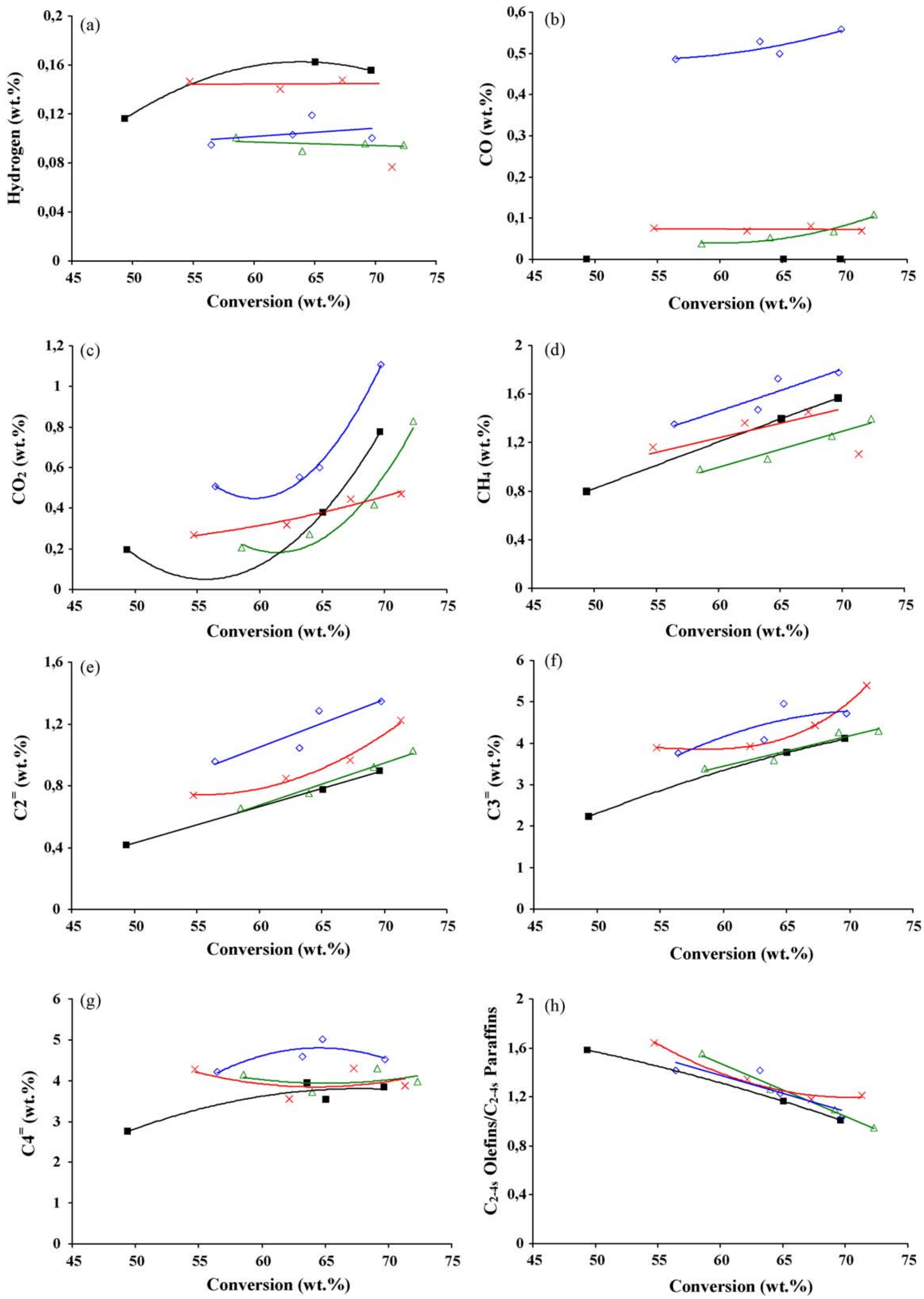


Fig. 2. (a) H_2, (b) CO, (c) CO_2, (d) CH_4, (e) ethylene, (f) propylene, (g) butylenes and (h) $C_{2\text{-}4s}$ olefins/$C_{2\text{-}4s}$ paraffins *vs.* conversion, for pure gasoil (■), gasoil + phenol (△), gasoil + acetic acid (◇) and gasoil + hydroxyacetone (×) mixtures with E-CAT.

Table 3
Hydrogen content and $(H/C)_{eff}$ ratio for the different feedstocks.

Feedstock	$(H/C)_{eff}$	H (wt %)
Pure gasoil	1.627	11.90
Gasoil/hydroxyacetone	1.582	11.60
Gasoil/acetic acid	1.576	11.55
Gasoil/phenol	1.541	11.35

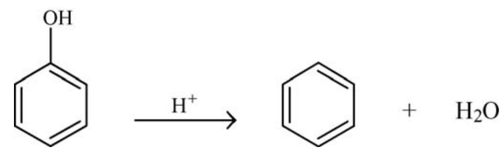
there are compounds with more proton affinity, such as nitrogenated compounds (Table 2). Thus, deactivation by site blocking and coke formation from oxygenated seems to be of a minor importance from these mixtures under tested conditions. However, it is true that in the presence of O-compounds, for higher conversions (higher CTO), an increase of the coke yield is observed (Fig. 1b), to values much closer to that noticed for pure gasoil, even if the amount of pure gasoil in the mixtures are lower. It seems that the higher coke contents are limiting the conversion of the gasoil present in the mixtures, which results in a reduction of the catalytic behaviour of the mixtures and, consequently, in a decrease of the difference between the mixtures conversion and the pure gasoil conversion (Fig. 1a).

Another issue related to the co-processing of oxygenate compounds is the reduction of hydrogen in the reaction medium. Indeed, with the present data, a reduction in the hydrogen yield was observed in the following order: hydroxyacetone > acetic acid > phenol (Fig. 2a). This order is in agreement with the $(H/C)_{eff}$ calculated for each feedstock as well as with the hydrogen amount present in the mixtures (Table 3).

A reduction in the hydrogen content will favour an increase in the product olefinicity. In line with this, an increase in the olefins/paraffin ratio ($C_{2\text{-}4s}$ olefins/$C_{2\text{-}4s}$ paraffins) from 1.3 to 1.5 was observed in the presence of oxygenated compounds (Fig. 2h). One could also expect that the low hydrogen content in phenol should be accompanied by a higher coke yield compared to the other model O-compounds. However, in this case, probably, the quantity of phenol added in the feed was not sufficient to result in a significant decrease of the hydrogen content of the feed. Moreover, the coke making seems to be governed by the amount of gasoil and a significant part of phenol is converted into benzene, as we are going to seen, a very stable hydrocarbon that does not increase the coke in FCC conditions [43].

The catalytic tests were performed in conditions close to that used in the commercial FCC units. Therefore, it was difficult to decouple the reactions of the model compounds from the several other reactions. Nevertheless, a qualitative more than quantitative study was done, in order to understand the O-compounds transformation. In the case of phenol co-feed, oxygenated compounds were found in the liquid effluents, therefore conversion values were determined for this oxygenated molecule.

The results obtained for the mixture gasoil/phenol, when compared to pure gasoil, showed an important increase in the gasoline yield (3 wt.% points at iso-conversion, Fig. 1f). A detailed analysis of the gasoline composition confirmed the presence of non-converted phenol. As already demonstrated by Adjaye and Bakhshi [11] and Gayubo et al. [15], phenol presents a relatively low reactivity when compared with other oxygenated compounds. Based on the quantity of unreacted phenol found in the liquid product, it was possible to estimate the phenol conversion (conversion = 1 − O-compound in product/O-compound in the feed). It was found an increase of the phenol conversion from 50% to 80%, with the increase of the CTO. An important increase of the benzene yield relatively to the pure gasoil and the other product mixtures were detected in the gasoline cut, when phenol was mixed with gasoil (Fig. 3a). The benzene yield increases with conversion while the phenol decreases, suggesting that dehydration of phenol to produce benzene and water is one of the reactions occurring (R.1). The formation of water can be clearly seen in Fig. 1e. Hence, co-processing of high amount of phenol (such as 10%) might be critical due to the benzene content limit in the gasoline (max. 1 vol.%).



Other phenolic compounds, namely methyl- and ethyl-phenol were observed in the gasoline cut (Fig. 3b). This shows that phenol can also be alkylated. The displacement of the negative charges due to the oxygen atom electronegativity makes the aromatic ring to become an electron acceptor that easily reacts to an electron donor, the olefins for example. Indeed, it was also observed a slight increase in the LPG in the presence of phenol (Fig. 1d). Perhaps, this slight increase in LPG could imply that phenolic ring attacked larger olefinic molecules, which then are cracked to form light ones. A similar increase in C3–C4 compounds has been previously observed by other authors [14,15,36].

When acetic acid is added to the gasoil, it was clear an increase in the fuel gas and LPG yields (Fig. 1c and d). Furthermore, CO and CO_2 also increased (Fig. 2b and c). Under conventional pyrolysis conditions, acetic acid is converted into methane (Fig. 2d) and CO_2

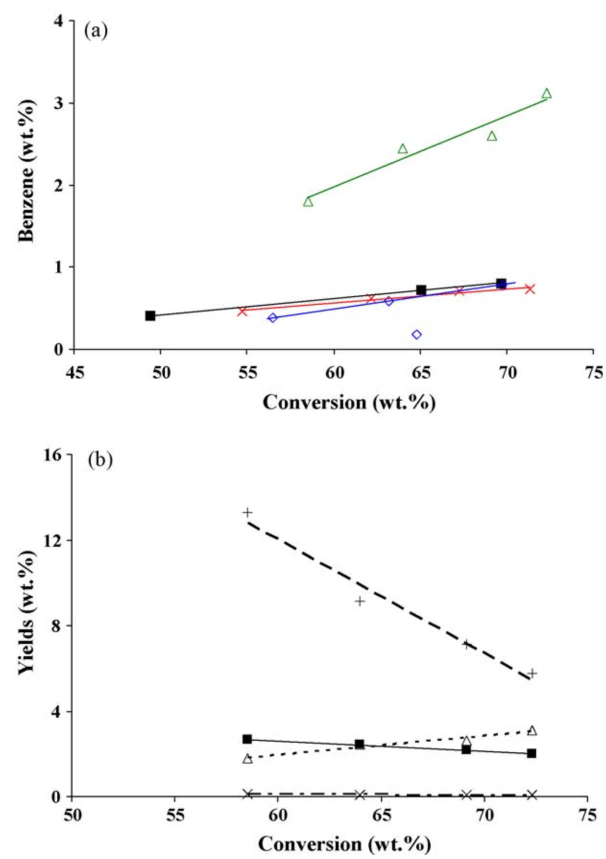


Fig. 3. (a) Benzene present in the gasoline cut *vs.* conversion for pure gasoil (■), gasoil + phenol (△), gasoil + acetic acid (◇) and gasoil + hydroxyacetone (×) mixtures, with E-CAT. (b) Phenol (+), benzene (△), methyl-phenol (■) and ethyl-phenol (×) *vs.* conversion, for gasoil + phenol mixture with E-CAT.

(R.2), as well as into ethylene (Fig. 2e) and CO ((R.3)–(R.5)) [37].

$$CH_3COOH \rightarrow CH_4 + CO_2 \quad (R.2)$$

$$CH_3COOH \rightarrow CH_2CO + H_2O \quad (R.3)$$

$$CH_2CO \rightarrow \,:CH_2 + CO \quad (R.4)$$

$$:CH_2 + \,:CH_2 \rightarrow C_2H_4 \quad (R.5)$$

The catalytic transformation of acetic acid also results in light olefins, such as ethylene, propylene (Fig. 2f) and butylenes (Fig. 2g), with the formation of CO_2 and to a lesser extent CO and water [16,38,39]. When co-processing up to 15 wt.% of an oxygenated feed (e.g. bio-oil), the CO_2 emissions are not seen as a problem, especially when the additional amounts come from a renewable source like biomass, which has an active participation in the carbon cycle. Furthermore, FCC units that operate in partial combustion mode generally have a CO boiler. For high amounts or full processing of an oxygenated feed, a new FCC concept coupled with CO_2 production or syngas production may be needed [44]. In fact, most of the CO and CO_2 produced in the FCC reactor from an oxygenated feed go to the fractionator column. The CO and CO_2 will increase in the regenerator if the coke formation also increases.

A slight decrease in gasoline yield (Fig. 1f) was still observed, but results just from a dilution effect due to the smaller quantity of gasoil present in this feed (93.4 wt.% of gasoil).

With the mixture of hydroxyacetone with gasoil, small increases in the fuel gas and LPG yields were observed compared to the pure gasoil (Fig. 1c and d), which are mainly due to an improvement of the ethylene and propylene production (Fig. 2e and f), respectively. The gasoline yield also registered a slight enhancement (Fig. 1f). This mixture did not exhibit outstanding difference in product yields from that of the gasoil mixture such as gasoline and water in the case of phenol and CO and CO_2 in case of acetic acid. However, considering the LPG yield based only on the percentage of gasoil present in the mixture as reference, an increase of LPG yield can be observed. The same comment can be made on the gasoline and fuel gas yields. No oxygenated compounds were observed in the liquid product. Corma et al. have tested hydroxyacetone (acetol) in the MAT at 500 °C. They observed acids, acetone and unidentified high-molecular-weight oxygenates/hydrocarbons as major products [40]. In the present work, the absence of oxygenated compounds may be due to oligomerization and/or subsequent conversion of acids and acetone.

3.2. E-CAT + ZSM-5

As observed for the pure E-CAT, in the presence of ZSM-5 additive there is also an increase in the conversion (Fig. 4a), and as consequence no enhance of the residual fractions is observed (Table 4), when the oxygenated compounds are added to the gasoil. In this case, considering the difference between the conversion for the mixture and the conversion calculated taken into account the percentage of gasoil present in the mixtures, the average increase in conversion obtained were 7.9, 4.7 and 4.2 wt.%, for phenol, acetic acid and hydroxyacetone, respectively. These increases are 21–48% smaller than the ones observed in the absence of ZSM-5 additive, but clearly demonstrate that the major part of O-compounds is not affecting adversely the conversion.

The ZSM-5 presence does not change the relative effect of the feeds in hydrogen production (Fig. 5a) observed for the E-CAT. Nevertheless, for the E-CAT + ZSM-5 mixture, the expected enhance of the olefins due to the reduction of the hydrogen formation for the O-containing charges were not detected, when compared with the pure gasoil (Fig. 5b). In this case, the decrease of

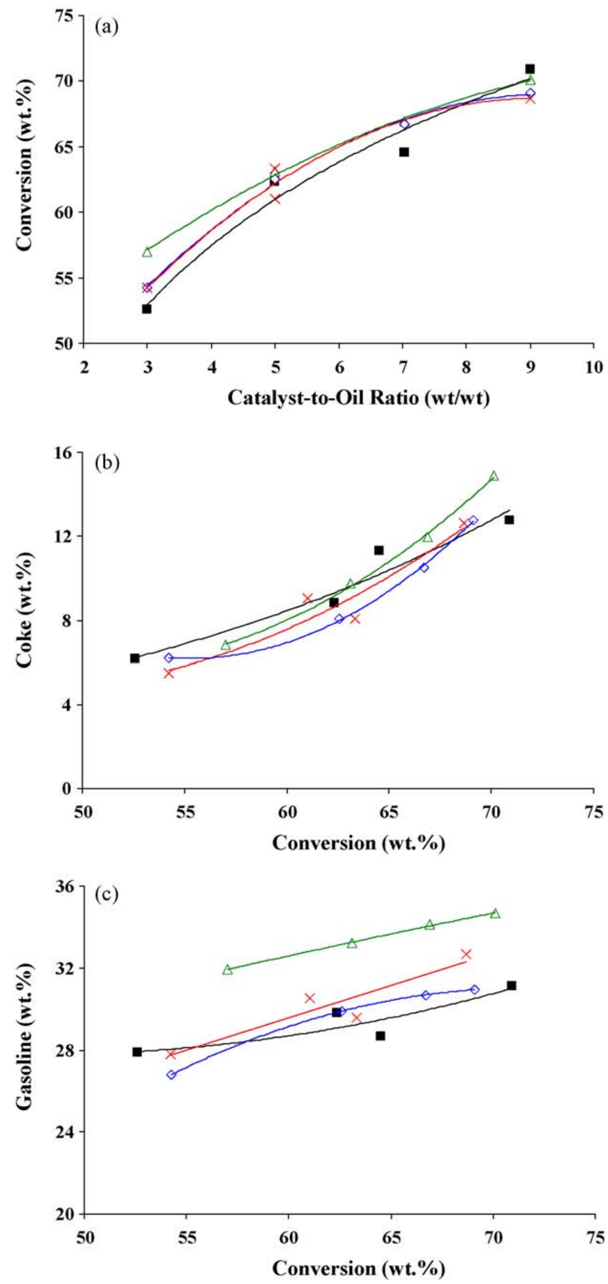


Fig. 4. (a) Conversin *vs.* CTO, (b) coke, (c) gasoline *vs.* conversion, for pure gasoil (■), gasoil + phenol (△), gasoil + acetic acid (◇) and gasoil + hydroxyacetone (×) mixtures with E-CAT and ZSM-5 additive.

the hydrogen content in the reactional medium was accompanied for a higher coke formation, principally in the presence of phenol (compound for which the mixture presents the lower hydrogen content, Table 3).

As well known, the ZSM-5 additives are added to the catalytic systems in order to convert the olefins present in the gasoline into light ones corresponding to the LPG range [32–35]. This tendency is well visible for all the feeds when comparing the gasoline and LPG yields obtained for the E-CAT and E-CAT + ZSM-5 presented in Table 4. For pure gasoil, the gasoline reduction is about 6.2 wt.% at conversion 63 wt.%. However, in the presence of acetic acid, hydroxyacetone and phenol the values are about 4.1, 5.2 and 4.8 wt.%, respectively. It is important to note that, although gasoline overcracking was indeed observed with E-CAT, the same does not hold in the presence of ZSM-5 (Fig. 4c). Indeed, the

Table 4
Product yields obtained at iso-conversion (63 wt.%) for all the feeds, considering the two catalytic systems.

Yields (wt.%)	E-CAT				E-CAT + ZSM-5			
	Pure gasoil	Gasoil/acetic acid	Gasoil/hydroxyacetone	Gasoil/phenol	Pure gasoil	Gasoil/acetic acid	Gasoil/hydroxyacetone	Gasoil/phenol
Coke	11.7	9.4	9.6	8.6	9.4	8.6	8.8	9.5
Fuel gas	2.7	3.7	3.0	2.5	3.3	3.7	3.4	2.8
CO	–	0.47	0.07	0.04	0.06	0.28	0.07	0.06
CO_2	0.25	0.54	0.35	0.17	0.38	0.62	0.44	0.34
LPG	12.4	15.7	14.0	13.2	20.4	20.7	19.7	16.7
Propane	1.42	1.63	1.56	1.39	1.98	1.89	2.02	1.70
Propylene	3.37	4.25	4.25	3.60	6.90	7.23	6.16	5.66
Butanes	4.20	5.13	4.40	4.22	5.61	5.29	5.85	4.67
Butylenes	3.39	4.73	3.82	3.91	5.83	6.28	5.60	4.67
Gasoline	35.8	33.4	35.9	38.1	29.6	29.3	30.7	33.3
H_2O	0.44	0.19	0.28	0.86	0.18	0.30	0.10	0.72
LCO	19.6	18.9	20.0	18.6	16.9	18.0	18.4	17.6
DO	17.2	17.7	16.8	18.0	19.9	18.6	18.4	19.0

increase in light olefins due to ZSM-5 is less pronounced in the presence of the O-compounds. Hence there are two possibilities: either in the presence of the O-compounds the ZSM-5 becomes less effective for the conversion of the gasoline cut olefins into lighter ones, or there are a smaller amount of olefins in the gasoline to be converted, when these compounds are present. As olefins content in the gasoline cut when oxygenates are mixed are equal or higher than olefins content in the gasoline from pure gasoil, the latest hypotheses is rejected. Therefore, this suggests a preferential interaction of such compounds with the ZSM-5 when compared to the E-CAT [41].

E-CAT + ZSM-5 mixture presents same products as those obtained with pure E-CAT, which indicates similar reactional pathways.

The results for the gasoil/phenol mixture in the presence of additive even showed a higher gasoline yield (Fig. 4c) relative to pure gasoil. Similar to the case of pure E-CAT, the detailed analysis of the gasoline composition, revealed the presence of non-converted phenol, methyl- and ethyl-phenol and an increase of the benzene with the conversion (Fig. 6a and b). An enhancement

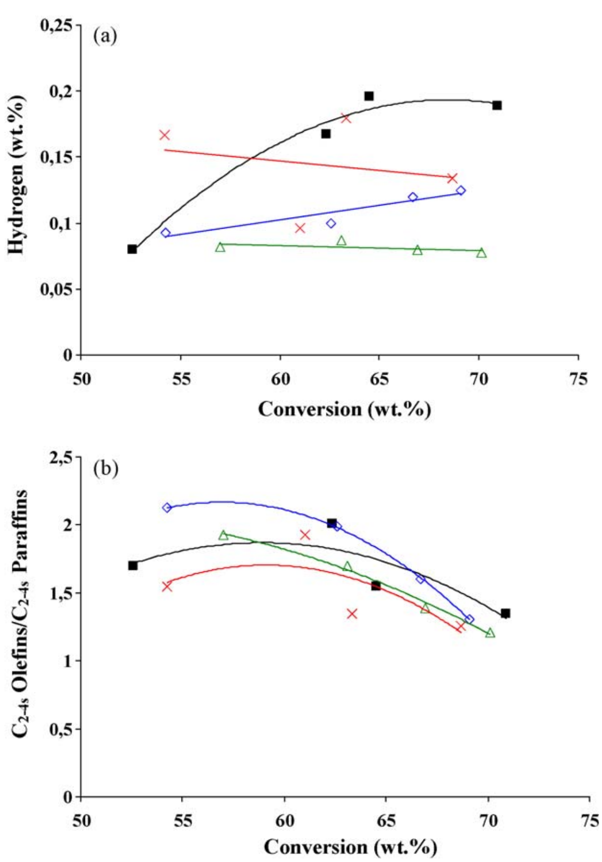


Fig. 5. (a) H_2 and (b) C_{2-4s} olefins/C_{2-4s} paraffins *vs.* conversion, for pure gasoil (■), gasoil + phenol (△), gasoil + acetic acid (◇) and gasoil + hydroxyacetone (×) mixtures with E-CAT and ZSM-5 additive.

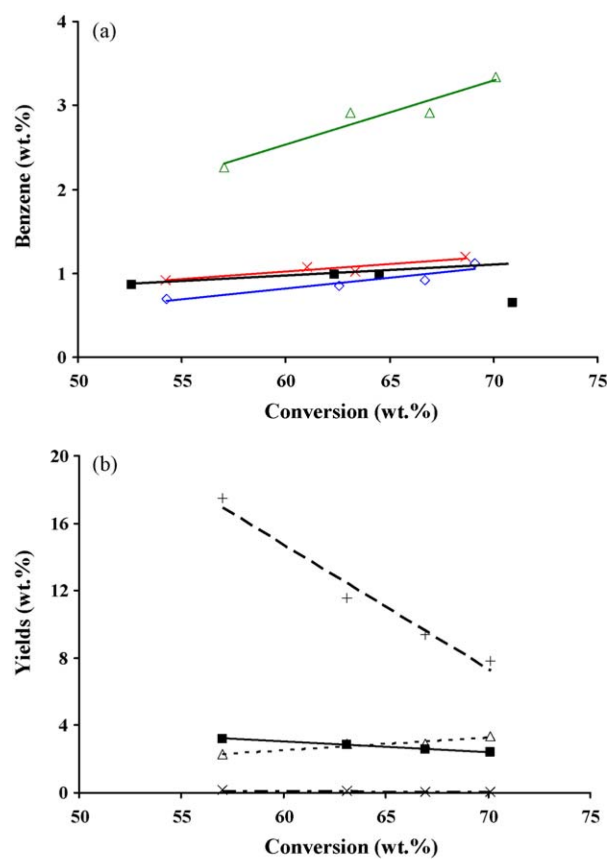


Fig. 6. (a) Benzene present in the gasoline cut *vs.* conversion for pure gasoil (■), gasoil + phenol (△), gasoil + acetic acid (◇) and gasoil + hydroxyacetone (×) mixtures, with E-CAT and ZSM-5 additive. (b) Phenol (+), benzene (△), methyl-phenol (■) and ethyl-phenol (×) *vs.* conversion, for gasoil + phenol mixture with E-CAT and ZSM-5 additive.

of the water content in the reactional effluent was also observed (Table 4). Thus, in the presence of ZSM-5, phenol alkylation and phenol dehydration to benzene also take place. The phenol conversion was 5–10% smaller than for pure E-CAT.

As for the pure E-CAT, the main products with acetic acid are fuel gas and LPG. An increase of the fuel gas yield for the acetic acid/gasoil mixture was observed (Table 4). However, comparing the LPG (Table 4) for the catalytic system E-CAT + ZSM-5, it is not evident the increase of the LPG yield when acetic acid is mixed with gasoil. This fact can be related to the attenuation of the ZSM-5 function in the presence of acetic acid, which results in a gasoline enhancement (Fig. 4c) with less LPG production relatively to the pure gasoil.

The hydroxyacetone/gasoil mixture E-CAT + ZSM-5 also shows same behaviour as E-CAT, slight increase in gasoline, fuel gas and LPG (Table 4). Although the LPG enhancement do not be clearly seen by the observation of Table 4, if one estimates the LPG produced from the gasoil present in the mixture (92 wt.%) as being $0.92 \times LPG_{pure\ gasoil}$ ($0.92 \times 20.4 = 18.8$ wt.%), it is obvious that the value found is smaller than the LPG yield obtained for the hydroxyacetone/gasoil mixture (Table 4), which confirms the increase of the LPG due to the hydroxyacetone transformation. Moreover, like for acetic acid/gasoil and phenol/gasoil mixtures, in this case the ZSM-5 function also seems to be attenuated.

Analyzing the coke yields obtained at iso-conversion for the pure E-CAT and for the E-CAT + ZSM-5 mixture (Table 4) for the catalytic tests with pure gasoil, it is possible to observe a decrease in the coke formation when ZSM-5 is present, which was already expected if one considers the porous system of Y (large pores zeolite) and ZSM-5 (intermediary pores zeolite) zeolites. The growth of coke molecules is limited by the size of the zeolites cages or channels [42]. While for the acetic acid and hydroxyacetone mixtures the same tendency is noticeable, when phenol is added to gasoil the coke formed for the E-CAT + ZSM-5 mixture is higher to that obtained for the pure E-CAT (Table 4). Moreover, observing Fig. 4b where is represented the coke yields for the E-CAT + ZSM-5 mixture, it is evident that the coke formed in the presence of phenol is always equal or superior when compared to that formed for the pure gasoil regardless the conversion level. For the acetic acid and hydroxyacetone mixtures, there is a reduction in the coke formation, as previously observed for the pure E-CAT. This increase in the coke yield in the presence of ZSM-5 additive when phenol is added to gasoil can be probably due to the existence of diffusional limitations. Contrarily to acetic acid and hydroxyacetone that are small and more flexible molecules, the diffusion of phenol molecules within of the narrow pores of the ZSM-5 zeolite seems to be hindered.

4. Conclusions

As a general trend, acetic acid, phenol or hydroxyacetone when mixed with a conventional gasoil and reacted over pure E-CAT increased the overall conversion, reduced the coke yield and increased fuel gas, LPG and gasoline. A reduction in the hydrogen yield was observed in the following order: hydroxyacetone $>$ ace-acetic acid $>$ phenol.

With phenol, marked increase in gasoline and water was observed. With acetic acid, light olefins, CO and CO_2 formation clearly increased. With hydroxyacetone, improvement of the ethylene and propylene production was observed. The above observations could be interpreted by the transformation of these model compounds themselves.

In the presence of E-CAT + ZSM-5 additive, the effect of O-compounds in co-processing was similar to that observed for the pure E-CAT. However, less gasoline was converted into LPG when acetic acid, hydroxyacetone and phenol were mixed with the gasoil. In the case of phenol, important coke yields were observed. The attenuation of the ZSM-5 effect in the presence of the O-compounds may be due to a preferential interaction of such compounds with the ZSM-5 when compared to the E-CAT.

Based on the obtained results, it is possible to conclude that up to 10 wt.% of the oxygenated compounds studied can be processed without major problems in a FCC unit, with the exception of phenol, which might be critical due to the benzene content specification in the gasoline (max. 1 vol.%).

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